AFCRL - 64 - 518

AUTOMATIC POLARIZATION APPARATUS

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Project 6694
Task 669406

Scientific Report No. 3

AF 19 (604)-8377

15 June, 1964

Prepared for

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

ABSTRACT

An apparatus which automatically measures and records anodic and cathodic polarization curves on semi-logarithmic coordinate paper is described. Conventional and potentiostatic measurements can be performed at potential sweep rates between 2×10^{-2} and 9×10^{2} volts/hour reproducible within $\pm$ 1%.

Polarization techniques have been used widely during the past sixty years to study the kinetics of metal dissolution and other reactions at metal/electrolyte interfaces.[1-3] The methods may be broadly divided into two categories: galvanostatic (constant current) and potentiostatic (constant potential). These measurements may be conducted using static or dynamic procedures. In the former, the electrode is allowed to reach steady-state before current or potential is measured, whereas during dynamic measurements, potential or current is varied continuously at a constant rate.

The above polarization methods and procedures have specific advantages and limitations. Galvanostatic polarization measurements are both inexpensive and easy to perform but cannot be used to characterize the kinetics of active-passive metals.[4] Potentiostatic polarization techniques may be used to determine the electrode kinetic behaviors of all systems but require complex and expensive circuitry. Static galvanostatic and potentiostatic polarization procedures yield steady-state data which are easy to analyze and interpret.[5] However, dynamic procedures

permit studies of systems which exhibit hysteresis[6] and time-dependent phenomena such as passivity.[7-8]

Dynamic potentiostatic polarization measurements are the most versatile since they are applicable to all systems. Further, if slow potential sweep rates are employed, steady-state polarization data can be closely approximated. Dynamic measurements are easily automated, permitting rapid data accumulation.[9]

Below, a versatile, automatic polarization apparatus using a dynamic potentiostatic method is described.

DESCRIPTION

The apparatus and its component parts are schematically illustrated in Figures 1 through 3. Figure 1 shows the complete circuit. A variable voltage signal generated by the programmer is applied to the auxiliary input terminals of an electronic potentiostat (Duffers, Inc., Model 600), which is connected to the electrode under study (working electrode). Potential and current are recorded simultaneously on semi-logarithmic coordinate paper with an XY recorder (Moseley "Autograf", Model 2D-2A). The potential between the working electrode and a saturated calomel

reference electrode is directly applied to the Y input terminals of the recorder (input impedance: 1 megohm). Current is measured by the potential across the precision resistor, R, ($\pm$ 0.5%) which is connected through a logarithmic voltage converter (Moseley Model 60D) to the X axis of the recorder.

The programmer, illustrated in Figure 2, produces a continuously changing voltage signal with a motor-driven potentiometer, B. The motor drive assembly consists of a D.C. motor, D; a stabilized rectifier speed control, E; and a 1000:1 variable gear reducer, C. These components permit a continuously variable speed range between 0.0014 and 17.5 rpm. The potential across the potentiometer, V, is supplied from the doubly-regulated zener voltage source, A, shown in Figure 3. This has a variable voltage output (-7 to +7 volts) with a 1 mv maximum AC ripple. A transistorized relay circuit, F, incorporated in the programmer, automatically disconnects the motor drive at any predetermined potential.

PERFORMANCE

The performance characteristics of the automatic polarization apparatus are summarized below:

1) This apparatus automatically measures and records anodic and cathodic polarization curves of normal and active-passive metals over a potential range of $\pm$ 6 volts at potential sweep rates between 2×10^{-2} and 9×10^{2} volt/hour. Potential sweep may be automatically arrested and held at any predetermined value. Measurements can be conducted through zero volts without the necessity of switching, which is usually associated with this operation.

2) The automatic characteristics of this apparatus permit high data output since an operator does not have to be present and the data are plotted automatically. By suitable calibration, the instrument is capable of directly plotting potential vs log current density curves over a current density range of 3.3 decades.

3) This apparatus is capable of yielding very accurate and reproducible polarization data. For example, anodic polarization measurements of 18 Cr - 8 Ni stainless steel in sulfuric acid are difficult to reproduce because of the time-dependent characteristics of this system.[4,8] With the above apparatus, a reproducibility (current density)

of ± 1% was achieved during six identical experiments. The ultimate accuracy and reproducibility of this apparatus are governed by the accuracy of its individual components (± 0.5 db for the logarithmic voltage converter, ± 0.2% full scale deflection of the XY recorder, and ± 0.25% linearity for the programmer output). Automatic curve recording also eliminates plotting errors.

In summary, it should be emphasized that this device does not obsolete conventional, manual polarization methods. It is advantageous for 1) rapid data output, 2) studies of time-dependent systems and 3) measurements of unusual electro-chemical phenomena (e.g., hysteresis) where high reproducibility is essential.

ACKNOWLEDGMENTS

This investigation was sponsored by the Geophysics Research Directorate, Air Force Cambridge Research Laboratories. The authors thank Dr. H. Ferguson, Duffers, Inc., Troy, N.Y., for his assistance in electronic design.

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FIGURES

Figure 1. Automatic Polarization Apparatus.

Figure 2. Programmer Circuit:

A.- Zener Voltage Source - see Figure 3.
B.- 500 ohm, 3600° potentiometers, $\pm$ 0.25% linearity.
C.- Variable gear reducer; Insco Corp., Model 00140.
D.- D. C. Motor, Bodine Electric Co., Model NSH-12 RG.
E.- Rectifier Control, Heller Type S12.
F.- Relay Circuit:
T = 2N2925 (General Electric Co.).
R = relay, Allied TSP 8.5 ma D. C., 1000 ohm.
L.- Motor Drive Indicator Lamp, 110 v.
S_1- Potential Arrest Switch
S_2- Reset Switch
V.- 0-10 v. D.C. voltmeter.

Figure 3. Zener Voltage Source:

C_1 = 4000 μF, 25 v.
C_2 = 500 μF, 10 v.
D_1 = 1N1622 Diode (General Electric)
D_2 = 10 v. 50 watt Zener Diode (50M10Z, General Electric).
D_3 = 6.8 v., 50 watt Zener Diode (50M6.8Z, General Electric).
L = Pilot Lamp, 12 v.
R_1 = 7.5 ohm, 25 watt
R_2 = 25 ohm, 5 watt
R_3 = 1000 ohm, 3600° potentiometer.
T = 12.6 v., 2 amp transformer.

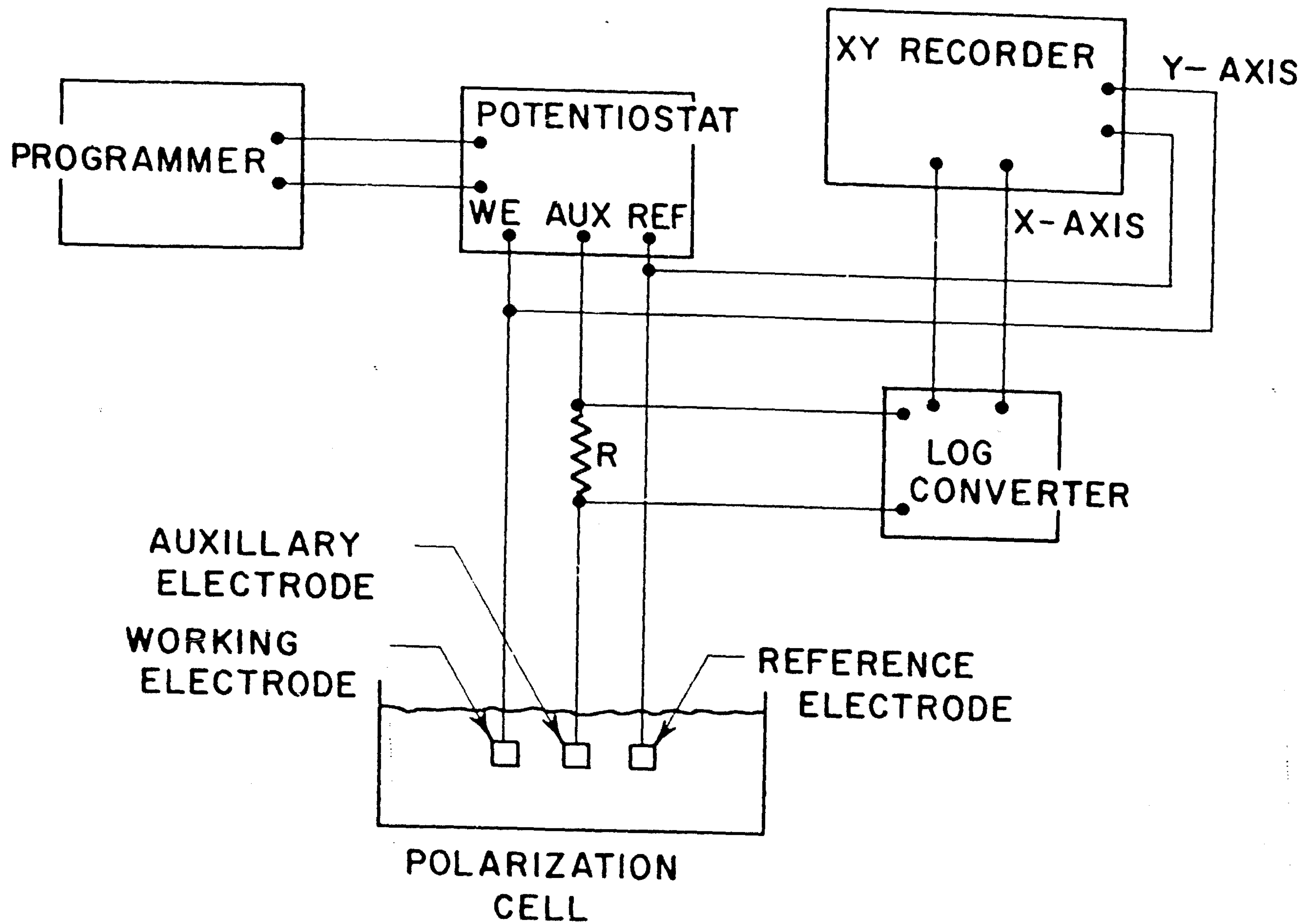
PROGRAMMER
POTENTIOSTAT
WE AUX REF
XY RECORDER
Y- AXIS
X- AXIS
LOG CONVERTER
R
AUXILLARY ELECTRODE
WORKING ELECTRODE
REFERENCE ELECTRODE
POLARIZATION CELL

FIGURE I

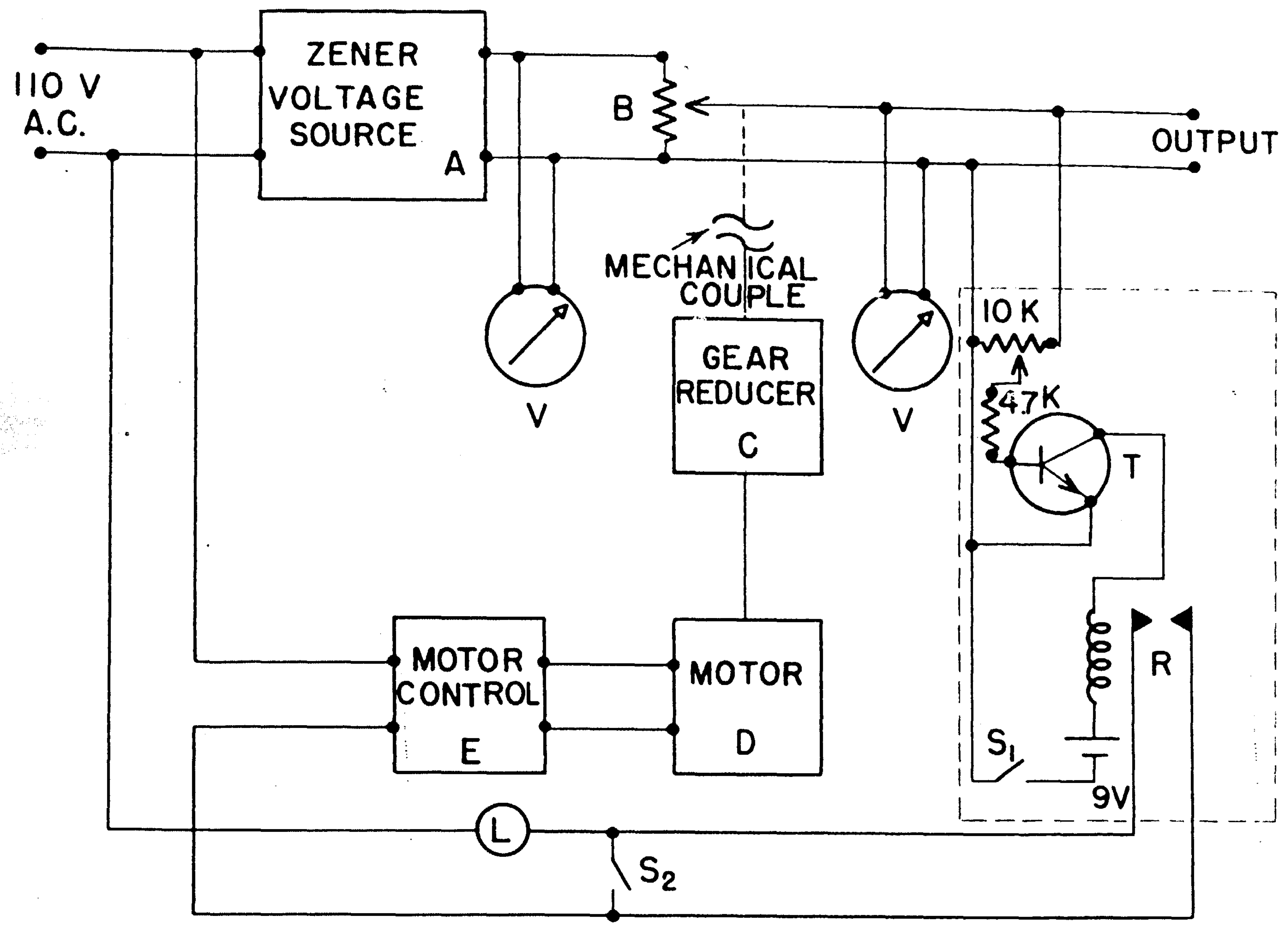
110 V
A.C.
ZENER
VOLTAGE
SOURCE
A
B
OUTPUT
MECHANICAL
COUPLE
V
V
GEAR
REDUCER
C
10 K
4.7K
T
F
R
S_1
9V
MOTOR
CONTROL
E
MOTOR
D
L
S_2

FIGURE 2

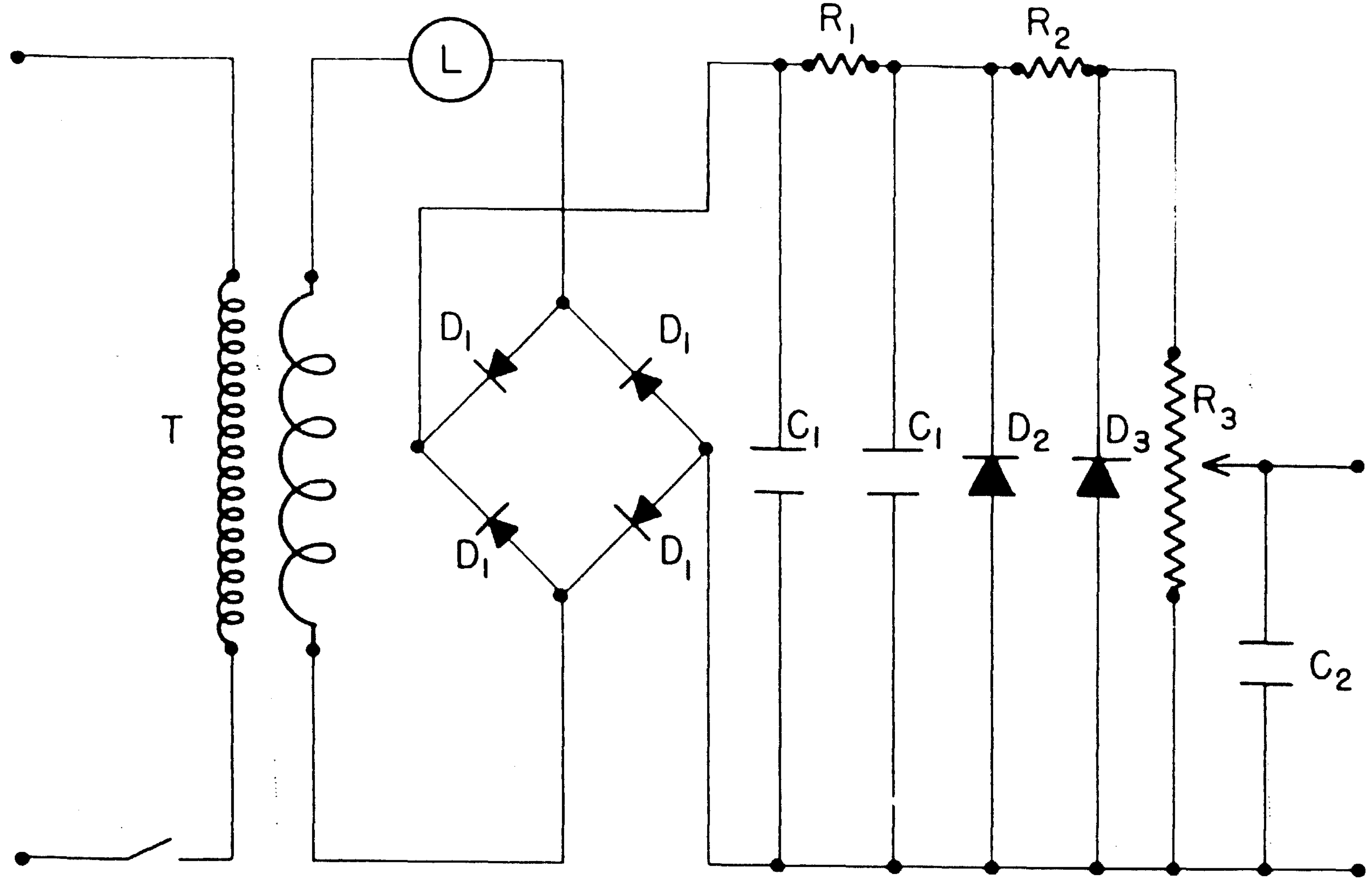

FIGURE 3

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1. Automatic operation for E vs log i curves
2. Variable sweep rate over 900 v/hr to 10^{-2} v/hr.
3. Increased accuracy and reproducibility

I. Project No. 6994
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